

# Lithium Dendrite Prevention for Lithium Batteries

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Project ID #bat275

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# Overview

## Timeline

- Start date: Oct. 2016
- End date: Sept. 2020
- Percent complete: 89%

## Budget

- Project funding
  - DOE share 100%
- Funding received in FY19: \$400k
- Funding received in FY20: \$400k

## Barriers

- Growth of lithium (Li) dendrites
- Low Coulombic efficiency (CE)
- Lack of mechanistic understanding

## Partners

- Argonne National Laboratory
- U.S. Army Research Laboratory

## Relevance/Objectives

- Enable Li metal to be used as an effective anode in rechargeable Li metal batteries for long cycle life.
- Explore various factors that affect ionic conductivity, Li Coulombic efficiency (CE), Li anode morphology, and battery performances.
- Develop hybrid polymeric composite electrolytes to protect Li metal anode.
- Develop low- to non-flammable polymer electrolytes and investigate effects of various flame-retardant solvents and polymers on battery performances.
- Investigate compatibility of such electrolytes with 4-V high-Ni NMC cathodes.

## Milestones

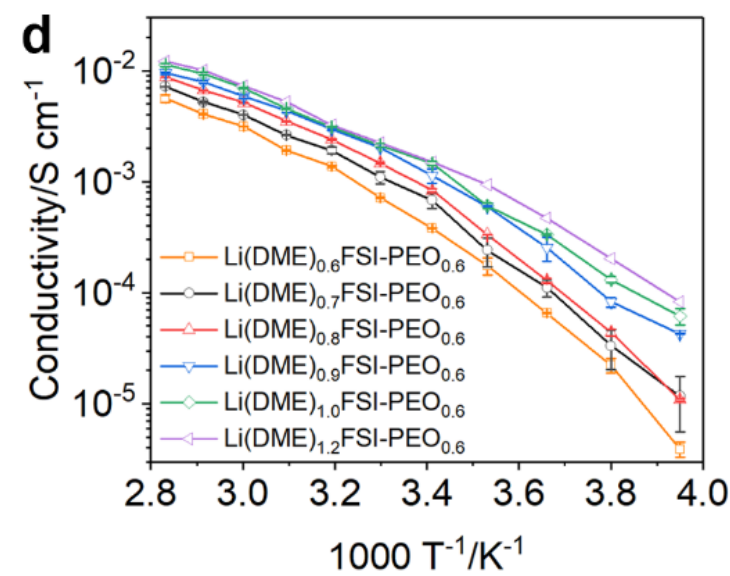
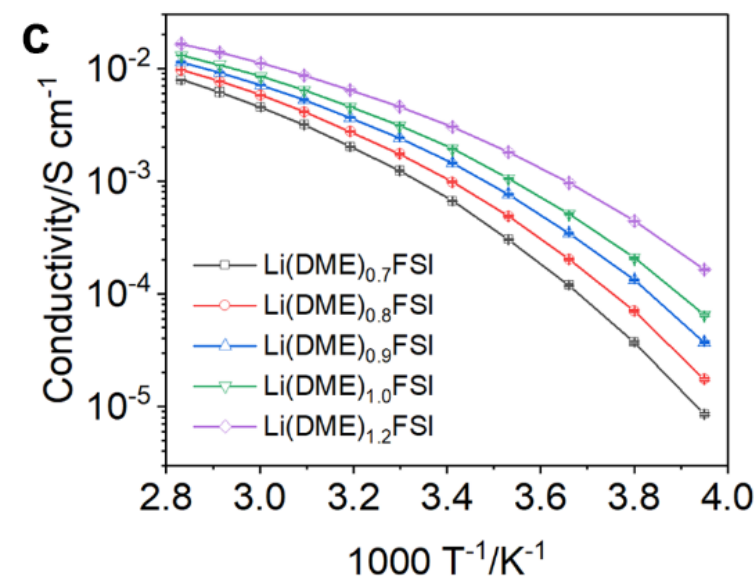
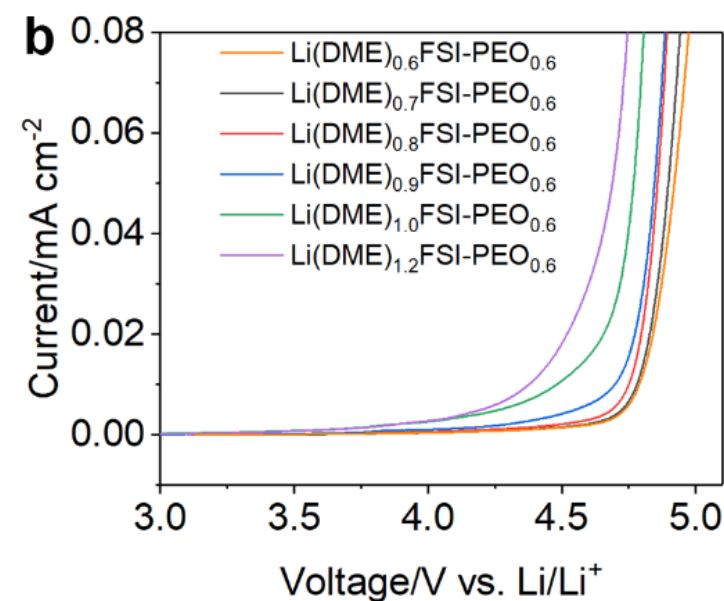
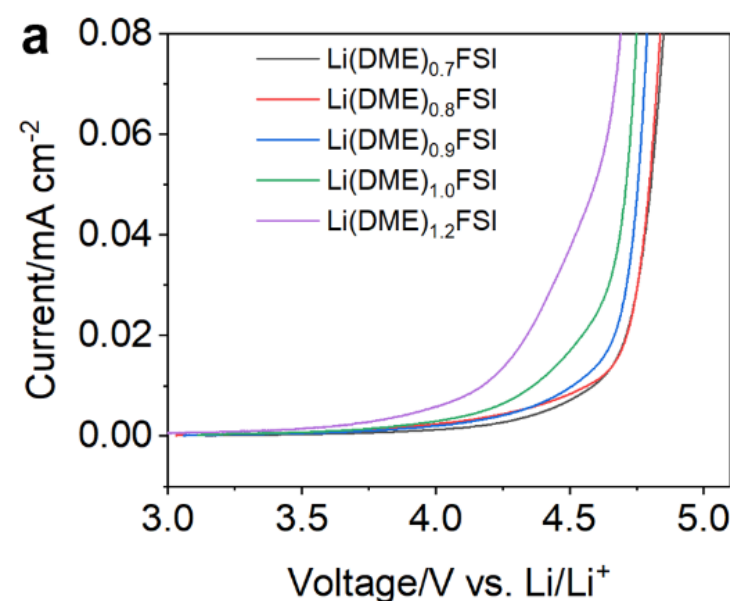
Date	Milestones	Status
June 2019	Develop an high concentration electrolyte (HCE) with Li CE > 98% and oxidation potential up to 4.4 V.	Completed
Sept. 2019	Achieve over 100 cycles for Li  NMC532 batteries with medium loading.	Completed
Dec. 2019	Develop polymerization method to get non-flammable polymer electrolytes with Li CE >98%.	Completed
March 2020	Characterize morphologies of SEI layers and deposited Li films at different current densities and deposition capacities.	Completed
June 2020	Investigate Li CE, deposited Li morphology and flammability of hybrid polymer composite electrolytes.	On track
Sept. 2020	(1) Achieve over 100 cycles for Li  NMC622 batteries with nonflammable hybrid polymer composite electrolytes. (2) Characterize compositions of SEI layers and deposited Li films at different test conditions.	On track

## Approaches

- Develop new hybrid polymeric composite electrolytes.
  - Develop polymer-in-‘quasi-ionic liquid’ electrolytes (PQILEs) with high oxidation stability and high conductivity.
  - Develop solid-state polymer-in-salt electrolytes (PISEs) to enable Li metal batteries cycled at high voltages.
- Develop low-flammable or nonflammable hybrid polymeric composite electrolytes.
- Develop effective artificial solid electrolyte interphase (SEI) for Li metal anode and optimization of liquid electrolyte.
- Investigate SEI and deposited Li with cryogenic transmission electron microscopy (cryo-TEM).
  - Investigate SEI and deposited Li formed in different electrolytes and under different test conditions. Characterize with other in-situ or ex-situ techniques, like scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), etc.

# Technical Accomplishments

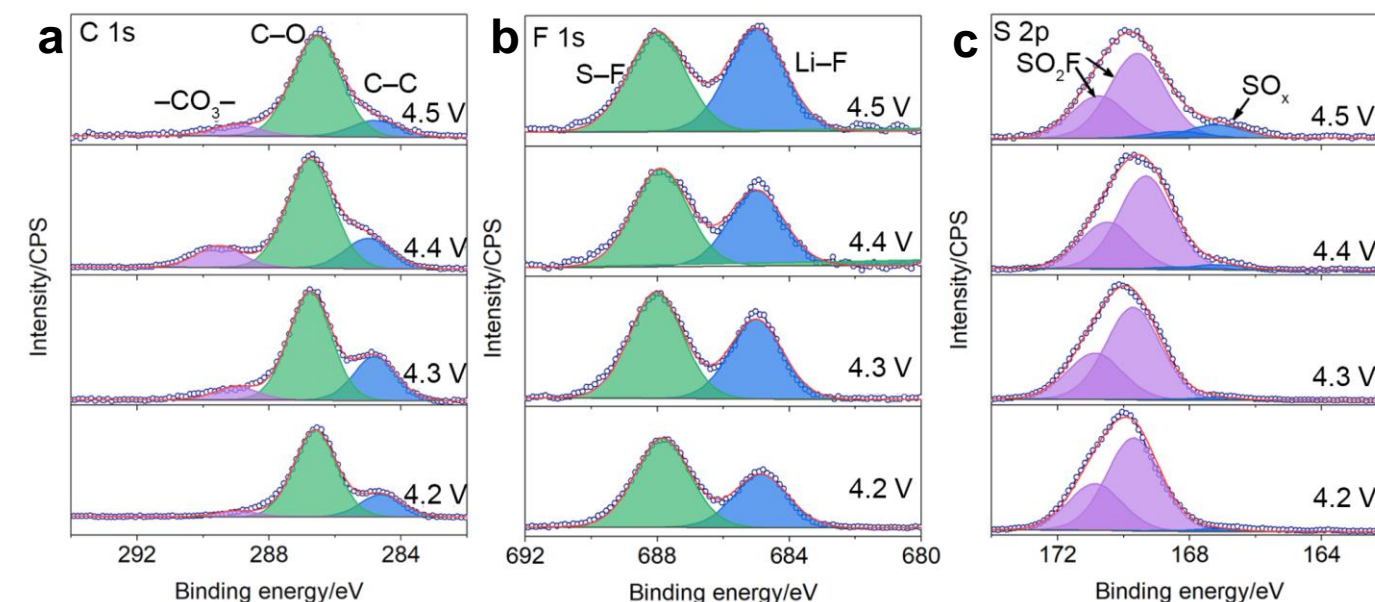
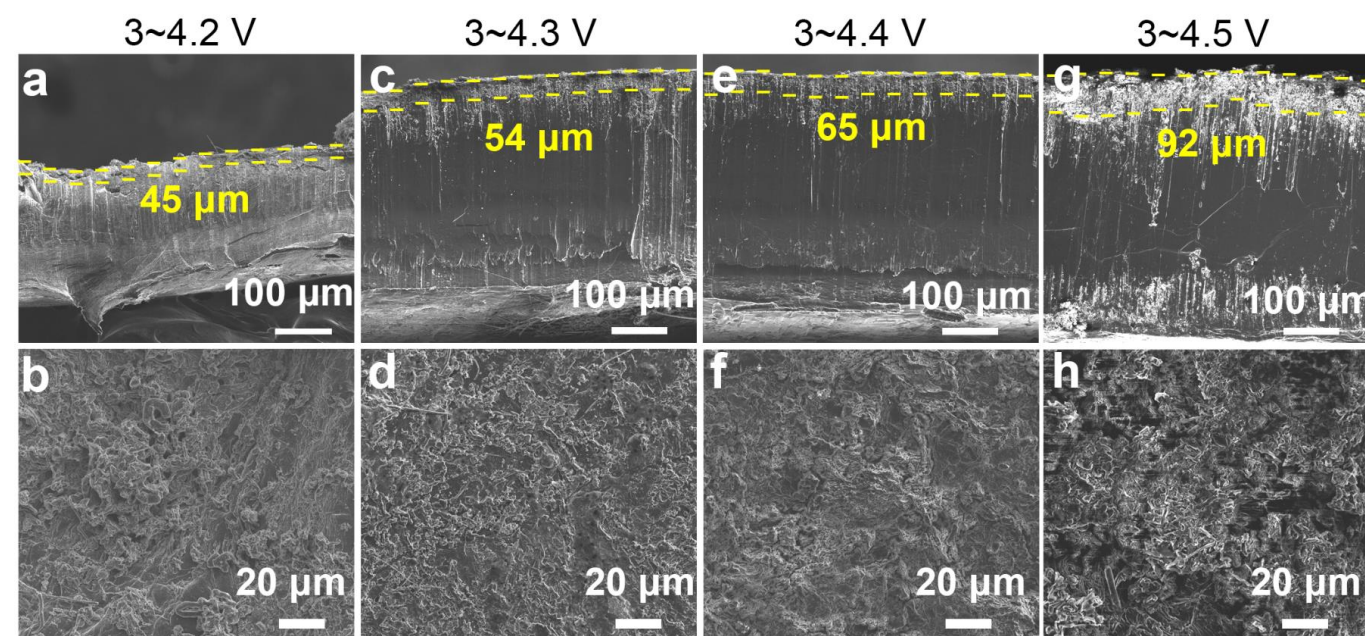
## Optimization of PQILEs with increased oxidation potential and ionic conductivity



- Anodic stability of the electrolytes increases monotonically with decreasing solvent content.
- Solvent content and ionic conductivity exhibit a positive correlation between.
- Li(DME)<sub>0.7</sub>FSI-PEO<sub>0.6</sub> is identified as an optimal PQILE due to its well-balanced electrochemical stability window and ionic conductivity.

# Technical Accomplishments

## Morphology of Li metal and SEI after cycling in Li||NMC333 cells with optimal PQILE at various charge voltages



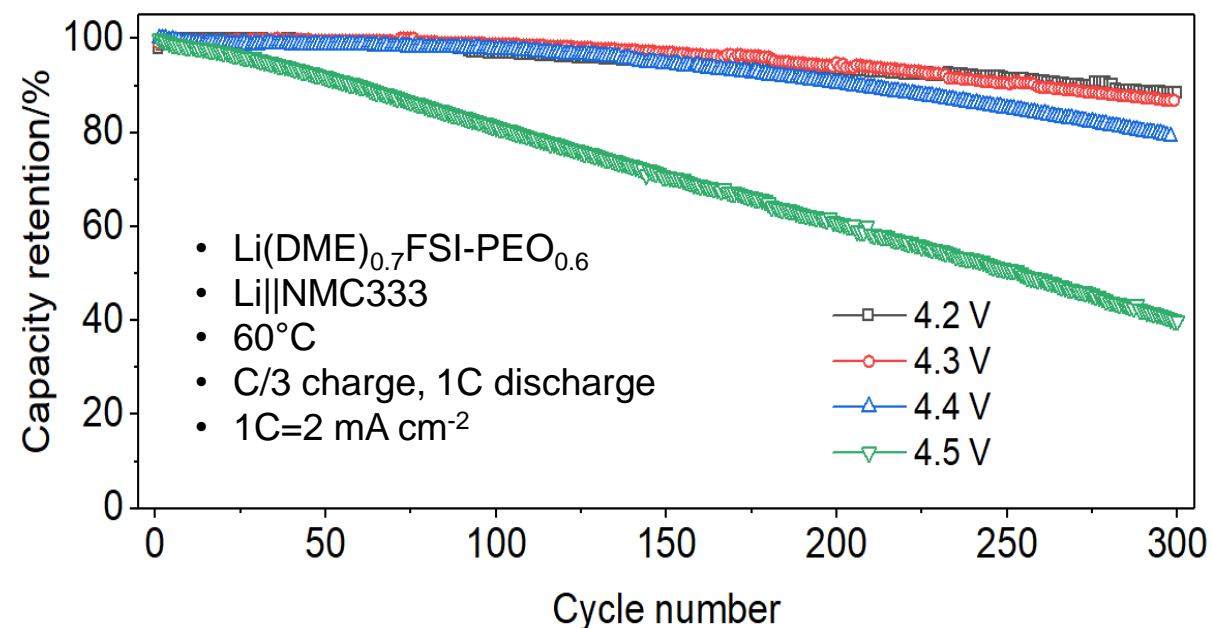
- Li metal corrosion layer become thicker with the increase of cut-off voltage.

- Anions continuously decompose to form LiF and sulfur-containing species in the SEI layer when the cutoff voltage reaches 4.5 V.

# Technical Accomplishments

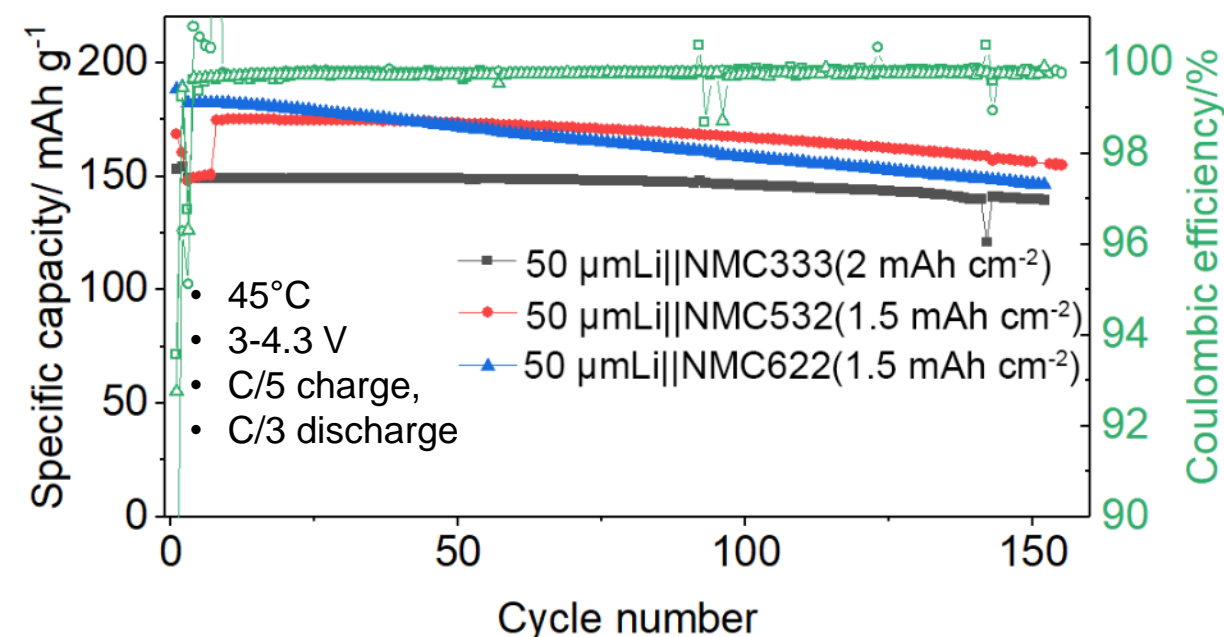
## Cycling performance of Li metal batteries with optimal PQILE at different conditions

Li||NMC333 cells under different charge cutoff voltages (4.2-4.5 V)



- PQILE enables Li||NMC333 to have stable cycling at a charge cutoff voltage up to 4.4 V.
- Charging to 4.5 V leads to fast capacity decay.

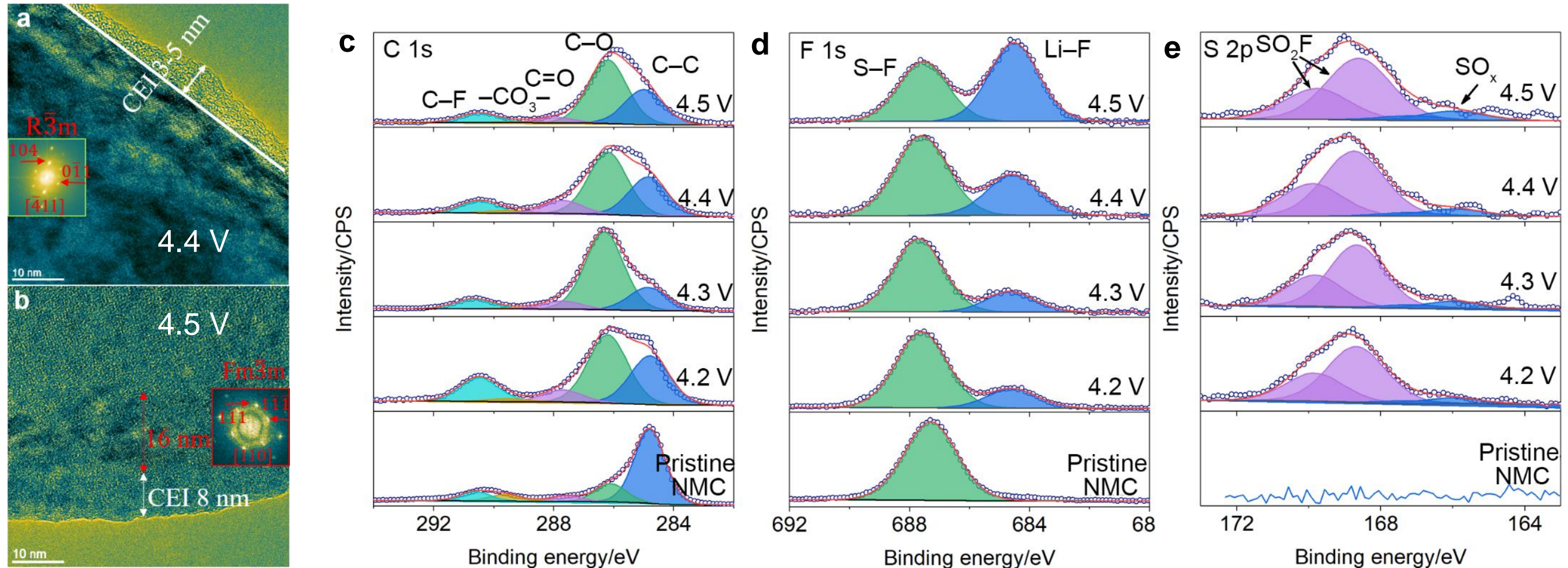
Li||NMC cells with different cathode materials at charge cutoff voltage of 4.3 V



- PQILE enables stable cycling of Li metal cells with Ni-rich cathodes NMC532 and NMC622 at 4.3 V.

# Technical Accomplishments

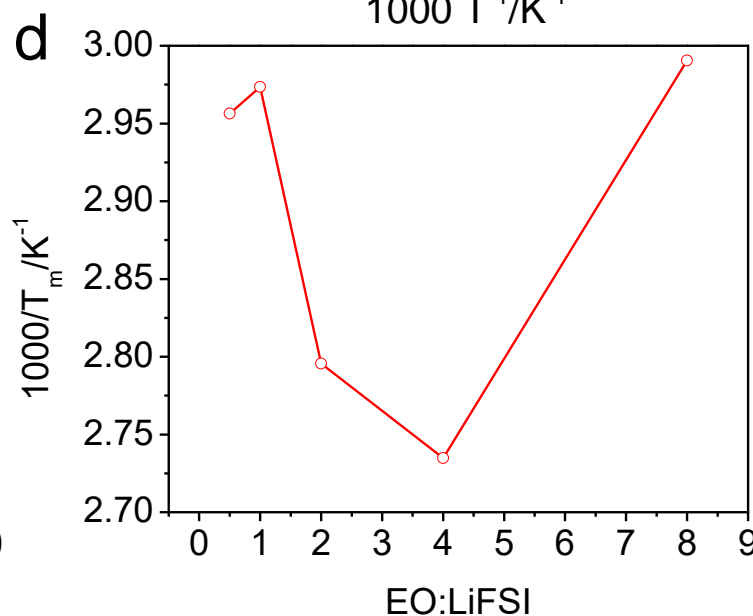
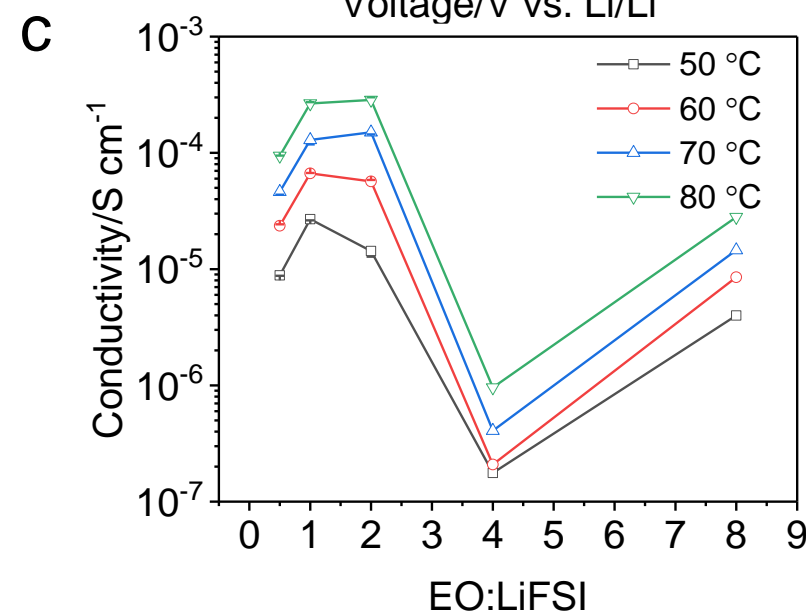
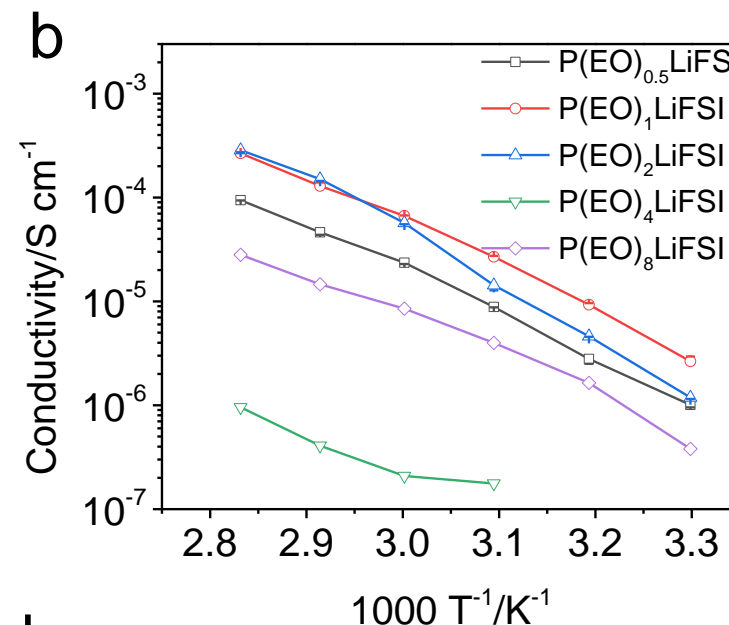
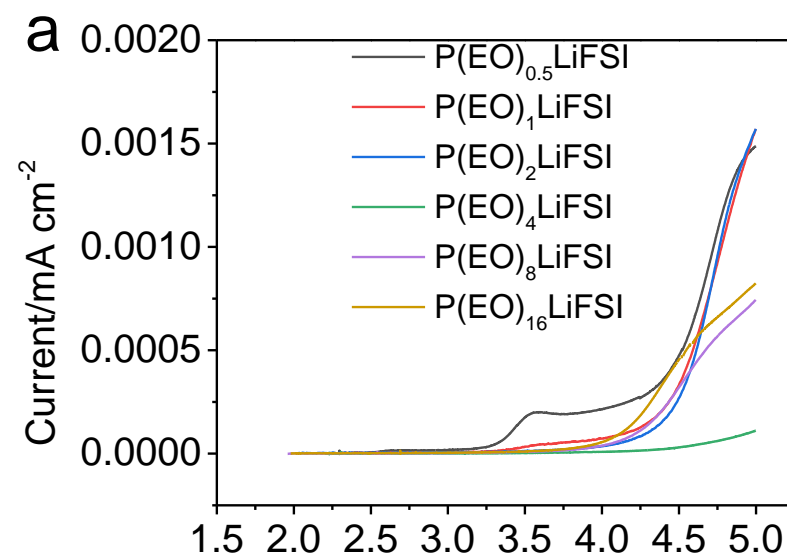
## Cathode electrolyte interphase (CEI) on NMC333 after cycling in PQILE at various voltages



- CEI is thin and layered structure of NMC333 was well maintained when charged to 4.4 V.
- More electrolyte decomposition was observed when charged to 4.5 V.

# Technical Accomplishments

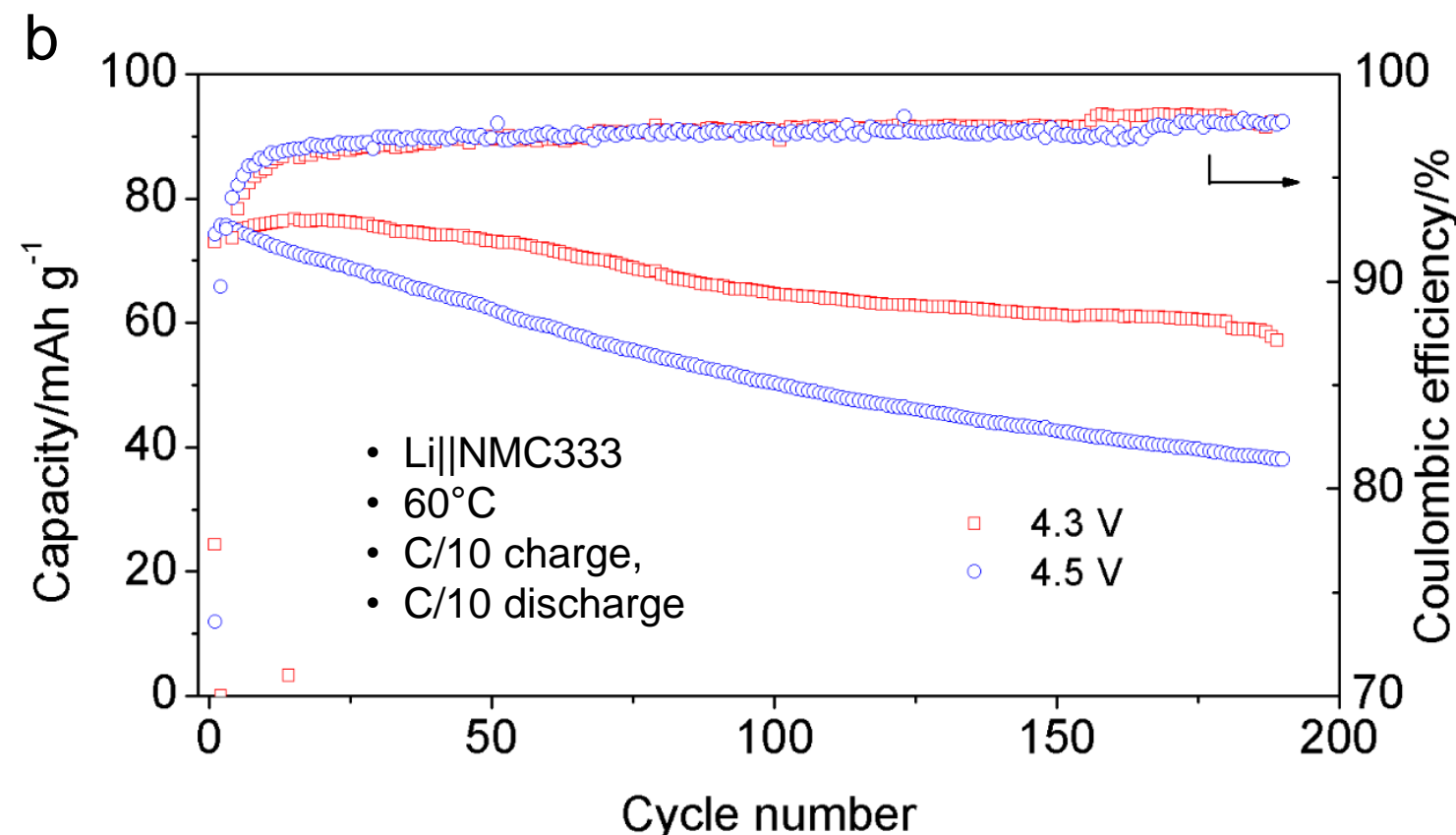
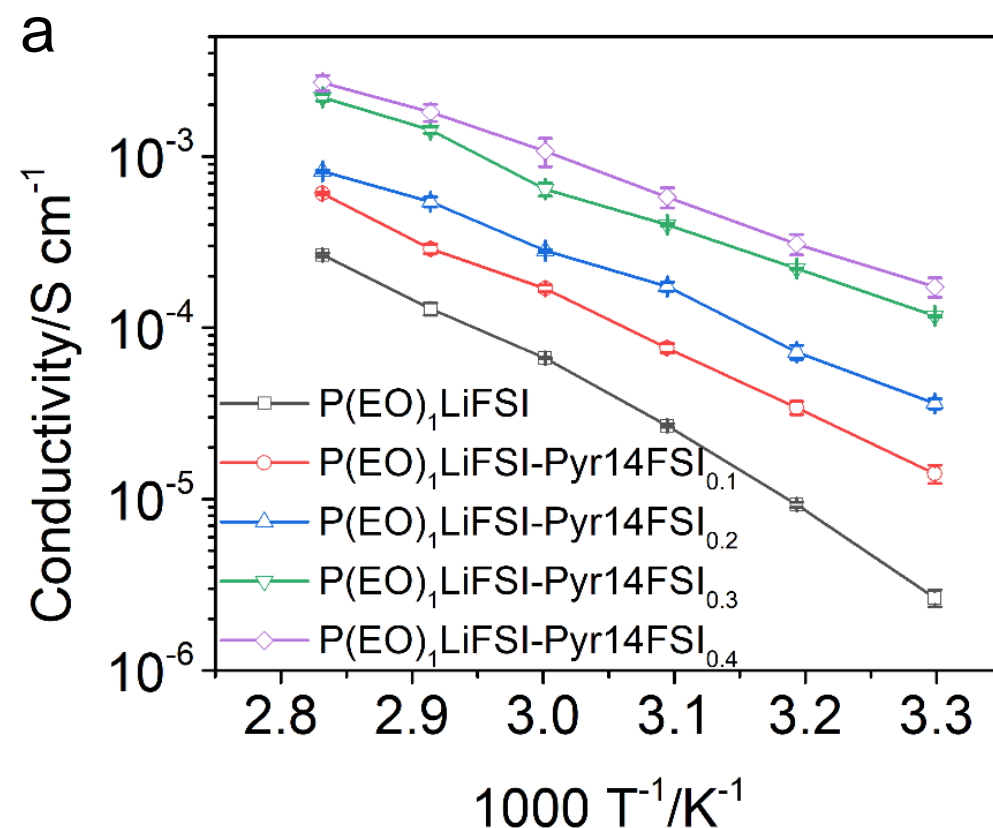
## Electrochemical stability of physical properties of PISEs



- PISEs were prepared by mixing PEO and LiFSI without solvent.
- PISEs with EO/Li ratio of 1~4 have higher oxidation voltage than those with EO/Li ratio > 4.
- P(EO)<sub>1</sub>LiFSI has the highest conductivity.
- PISE with lower melting temperature has higher conductivity.

# Technical Accomplishments

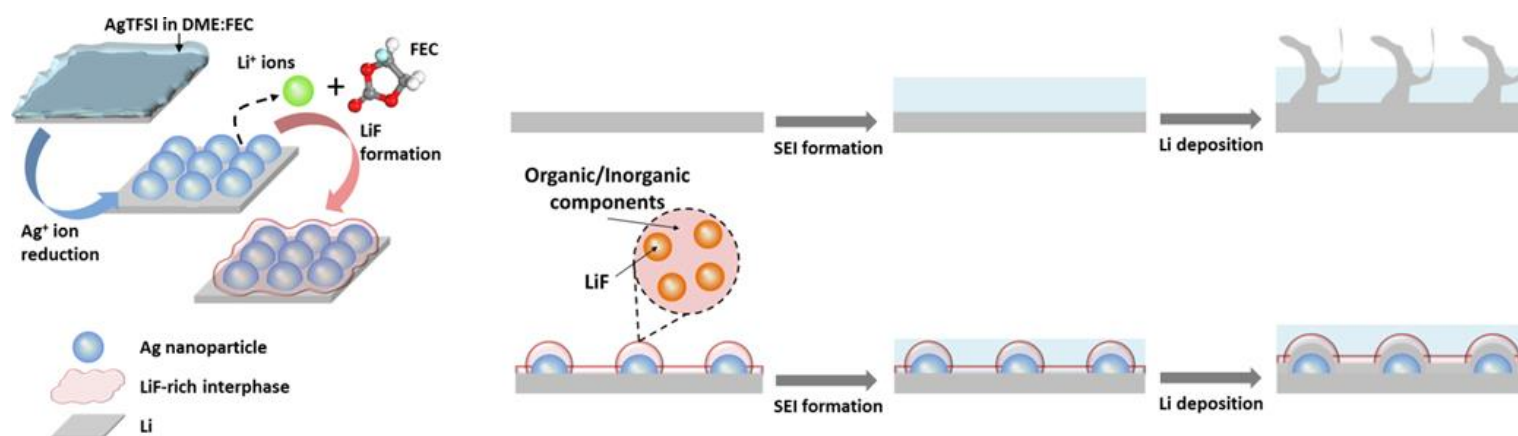
## Conductivity and cycling performance of ionic liquid plasticized PISEs



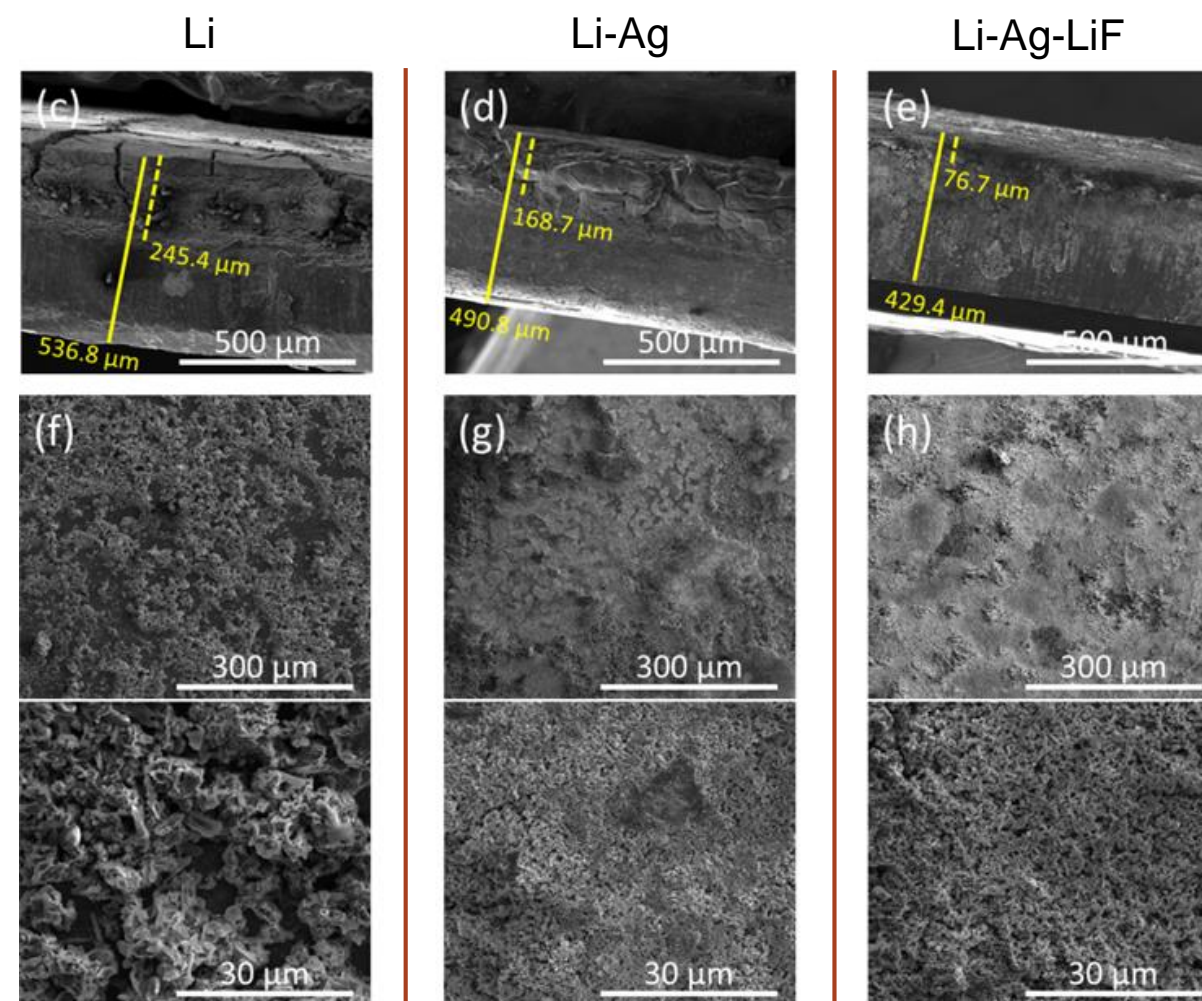
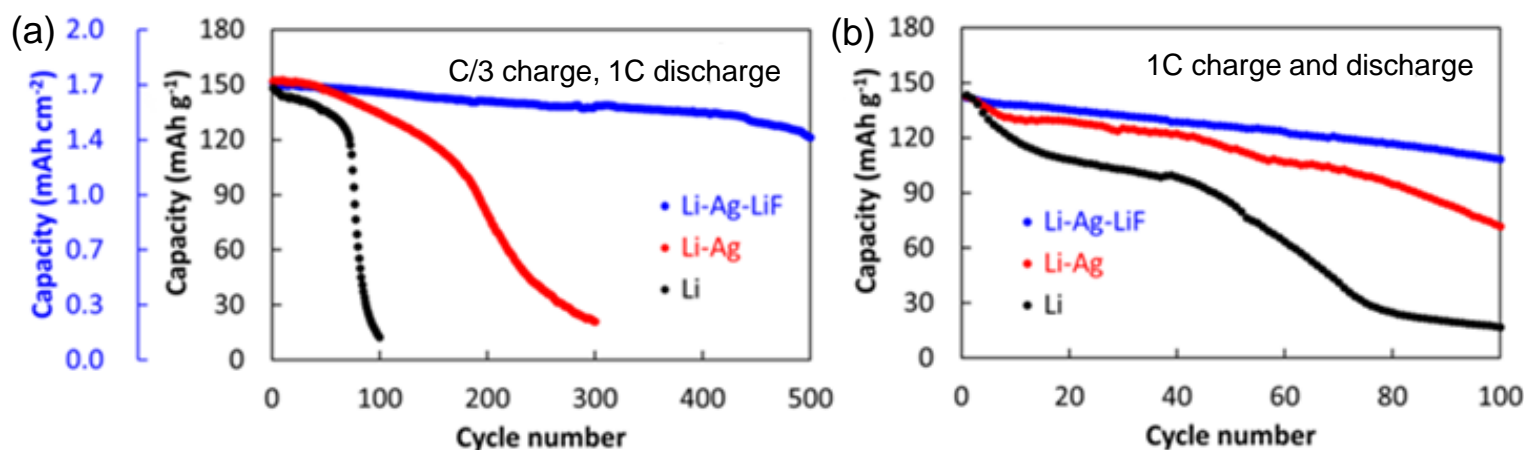
- The conductivity of P(EO)<sub>1</sub>LiFSI-Pyr14FSI<sub>0.4</sub> increases more than one order of magnitude as compared with that of P(EO)<sub>1</sub>LiFSI.
- Quasi-solid state Li||NMC333 cell using P(EO)<sub>1</sub>LiFSI-Pyr14FSI<sub>0.4</sub> electrolyte exhibits stable cycling performance with a cut-off voltage up to 4.3 V.

# Technical Accomplishments

## Ag-LiF artificial SEI to protection Li metal anode



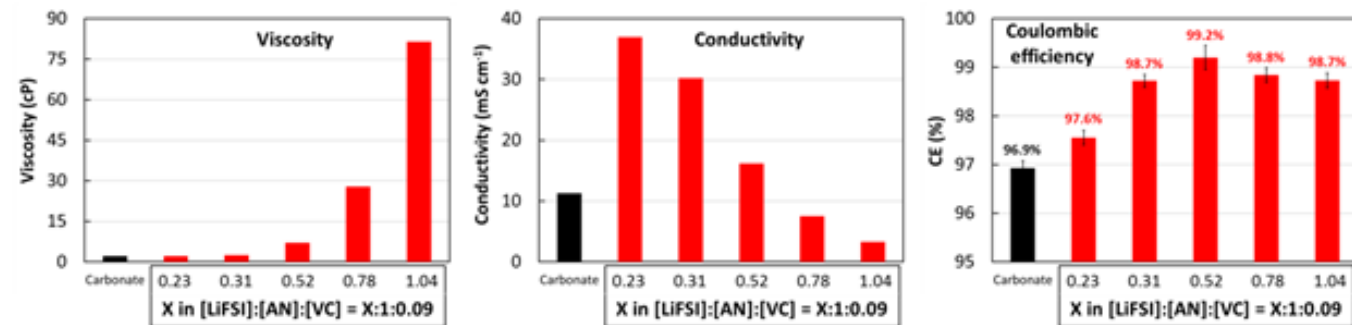
Li||NMC333 with LiPF<sub>6</sub>/EC-DMC



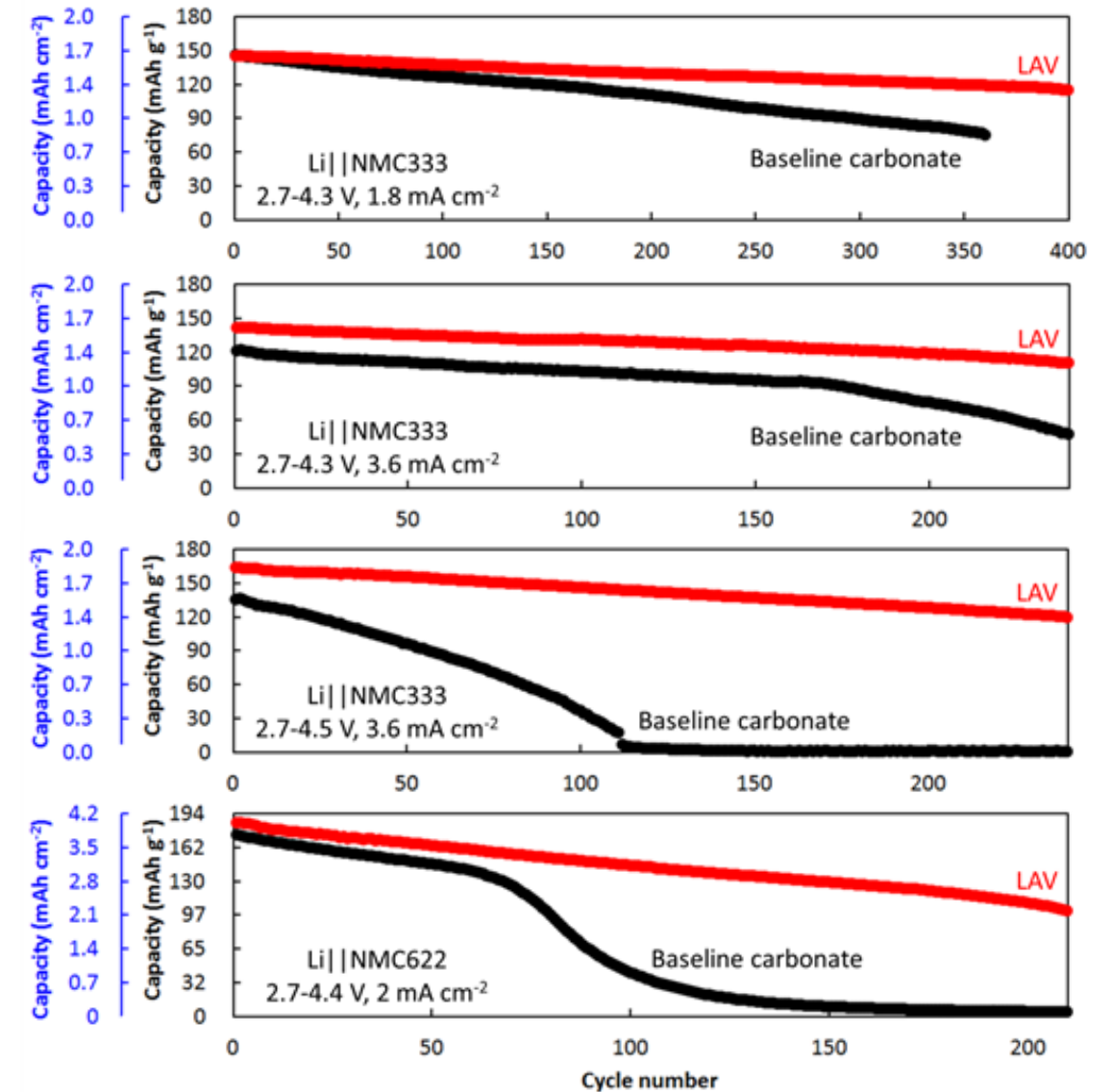
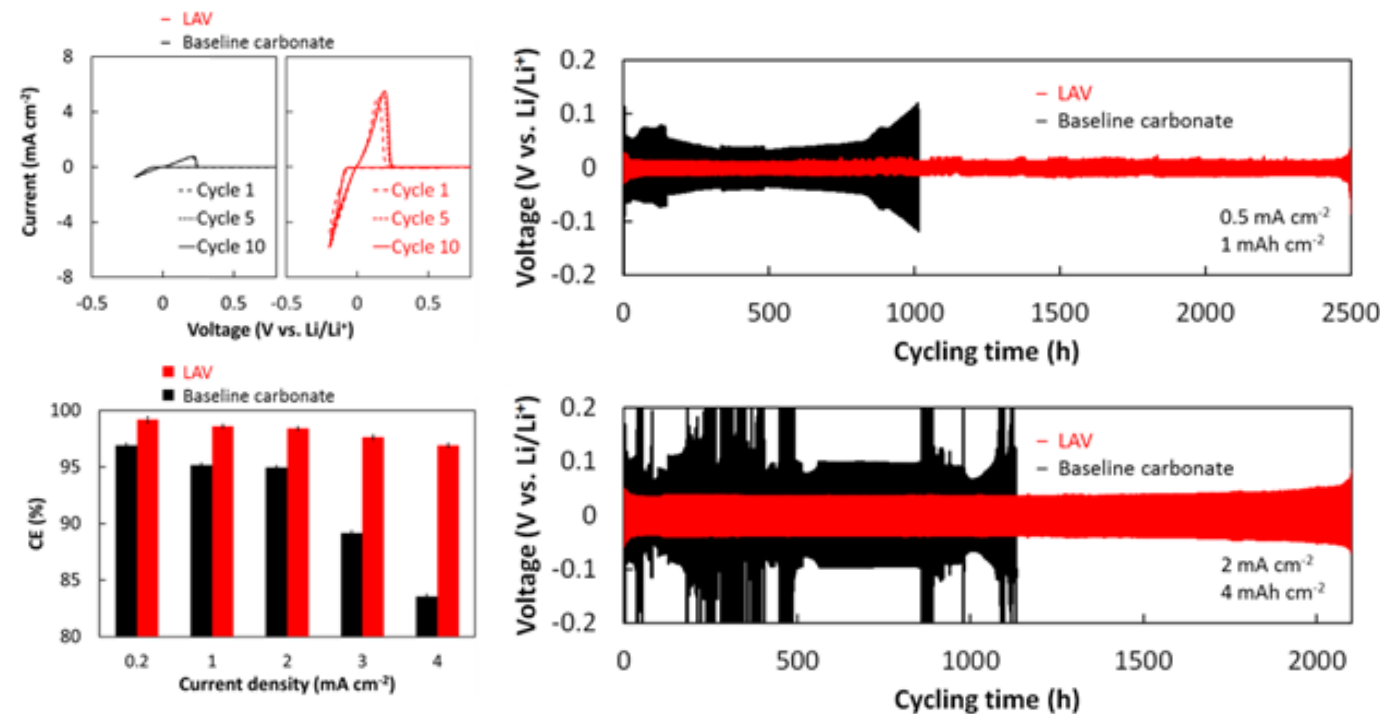
- Li-Ag-LiF coating enables Li||NMC333 cells to show the best cycling performance among selected Li anodes.
- Both Li-Ag and Li-Ag-LiF coated Li exhibit smoother morphology than those of pure Li after long-term cycling.
- Enhanced stability of Li metal anodes can be attributed to the synergetic control of nucleation and SEI.

# Technical Accomplishments

Vinylene carbonate (VC) additive enables acetonitrile (AN) based high concentration electrolytes for high power Li metal batteries



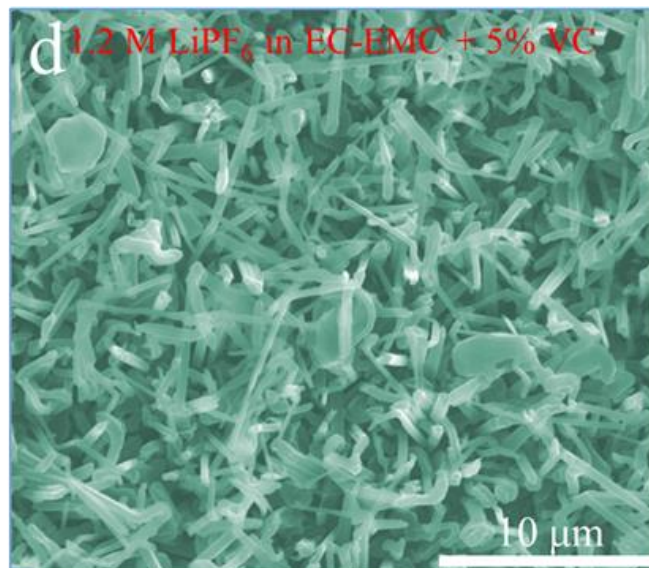
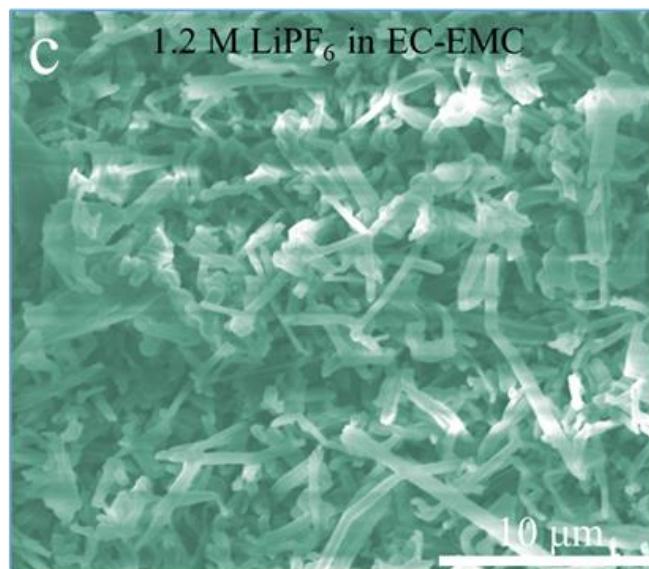
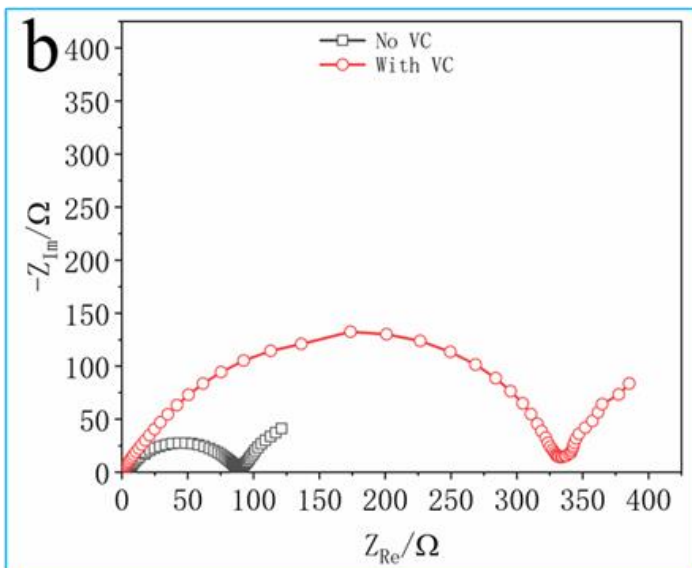
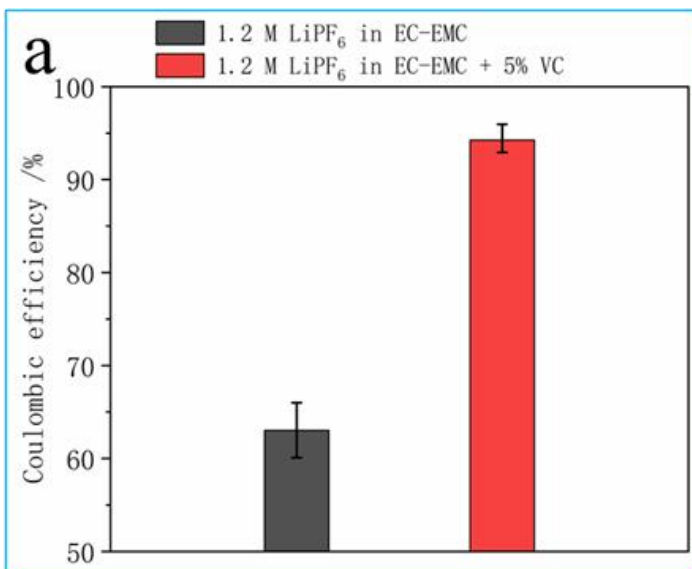
LAV = 0.52LiFSI-1AN-0.09VC; E-baseline = 1 M LiPF<sub>6</sub> in EC-DMC + 10% FEC



- LVA shows high Li CE, excellent stability with Li metal, and superior cycling performance in Li metal batteries at high voltages and high current densities.

# Technical Accomplishments

## Influence of VC on Li CE, impedance and Li deposition morphology

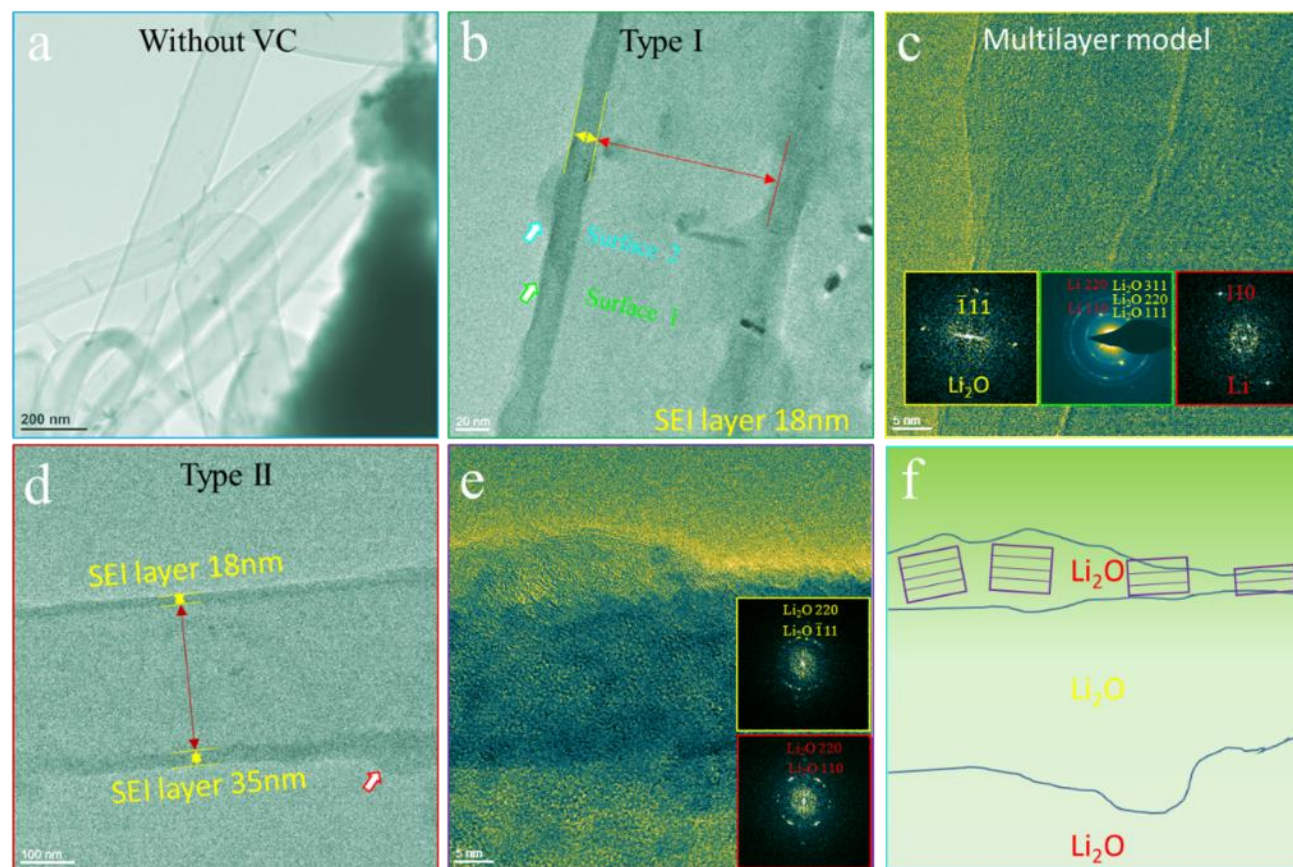


- 1.2 M LiPF<sub>6</sub> in EC:EMC (3:7 by wt.)
- 1.2 M LiPF<sub>6</sub> in EC:EMC (3:7 by wt.) + 5 wt.% VC
- Addition of VC in LiPF<sub>6</sub>/EC-EMC leads to significantly improved Li CE but also increases the cell impedance.
- No significant morphological difference was observed for electrochemically deposited Li (EDLi) in the electrolytes with and without VC additive.

# Technical Accomplishments

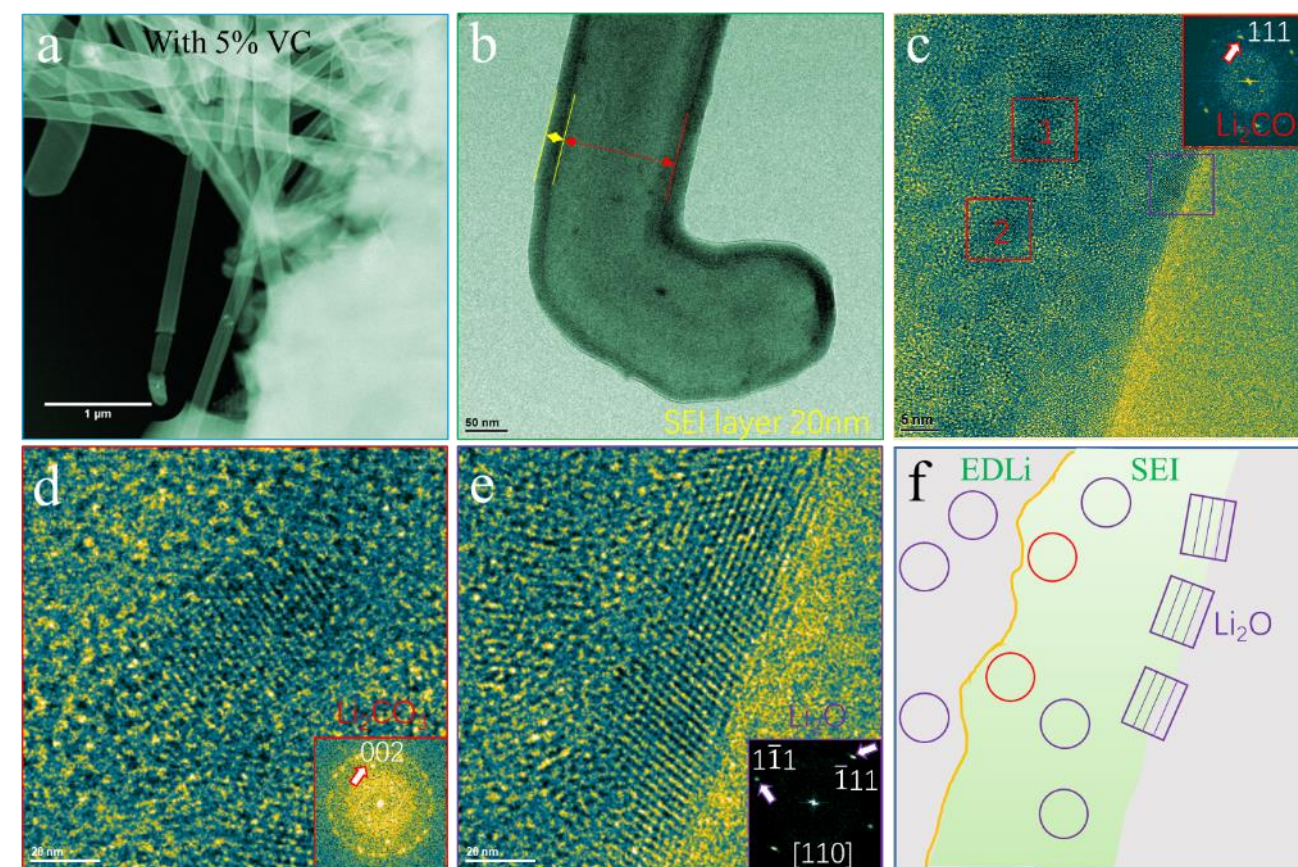
## Effect of VC additive on structure and composition of SEI formed on EDLi in $\text{LiPF}_6/\text{EC-EMC}$ electrolyte determined by cryo-TEM

1.2 M  $\text{LiPF}_6$  in EC:EMC (3:7 by wt.)



- Without VC, EDLi is featured by a combination of fully oxidized Li with  $\text{Li}_2\text{O}$  SEI layer and pure Li metal with multilayer nano-structured SEI.

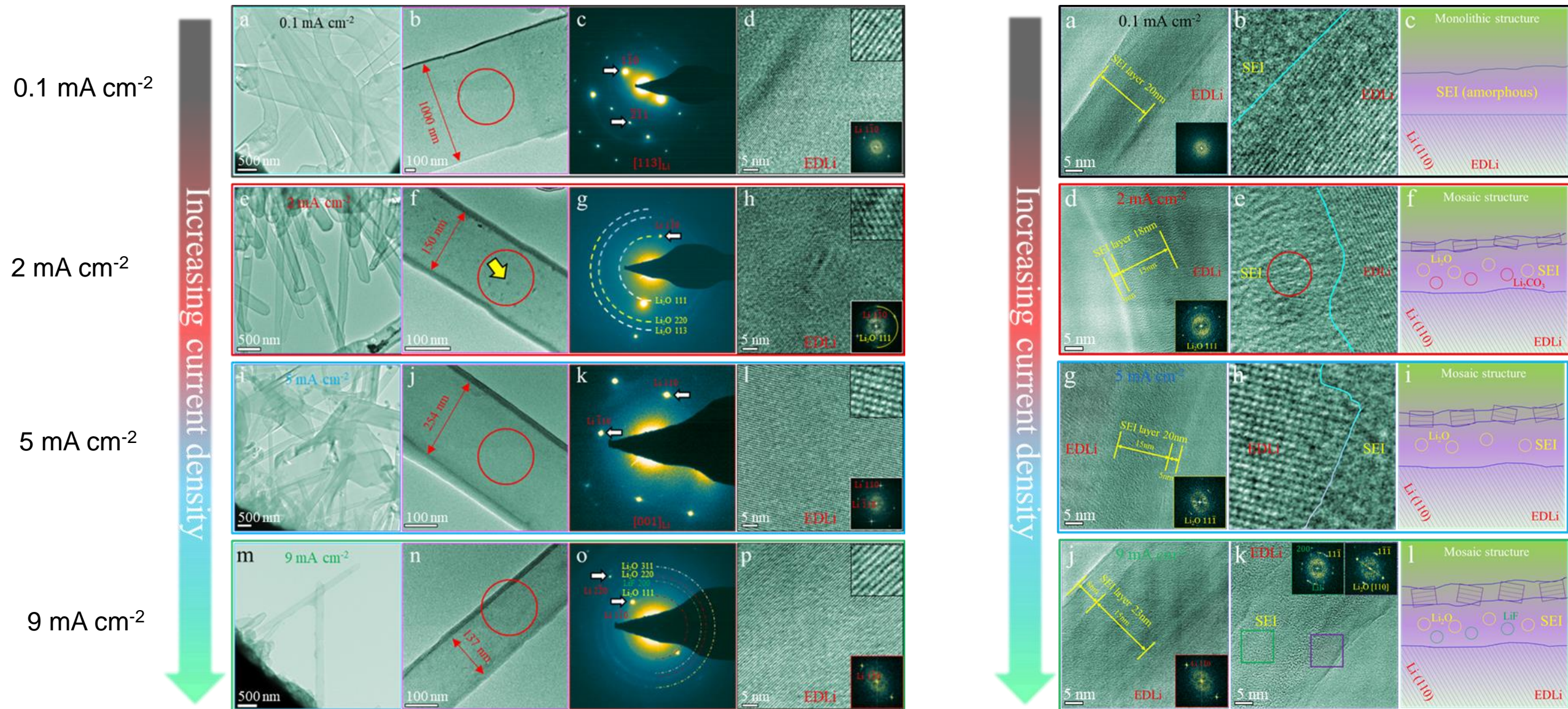
1.2 M  $\text{LiPF}_6$  in EC:EMC (3:7 by wt.) + 5 wt.% VC



- With VC, EDLi is slightly oxidized with the SEI being a nanoscale-mosaic like structure comprised of organic species,  $\text{Li}_2\text{O}$  and  $\text{Li}_2\text{CO}_3$ .

# Technical Accomplishments

## Morphology of EDLi and structure of SEI at different current densities in $\text{LiPF}_6/\text{EC-EMC} + \text{VC}$ electrolyte



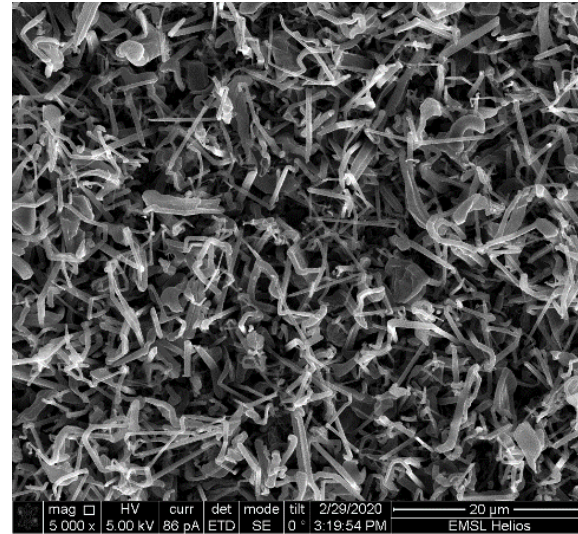
- Deposited Li is single crystalline Li metal independent of current density.
- SEI changes from monolithic structure to mosaic structure with increasing deposition current density.

# Technical Accomplishments

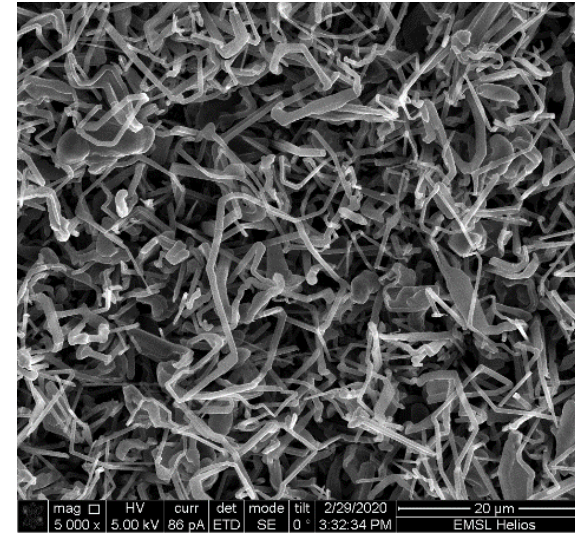
## Influence of deposition capacity on morphology of deposited Li metal

Top view

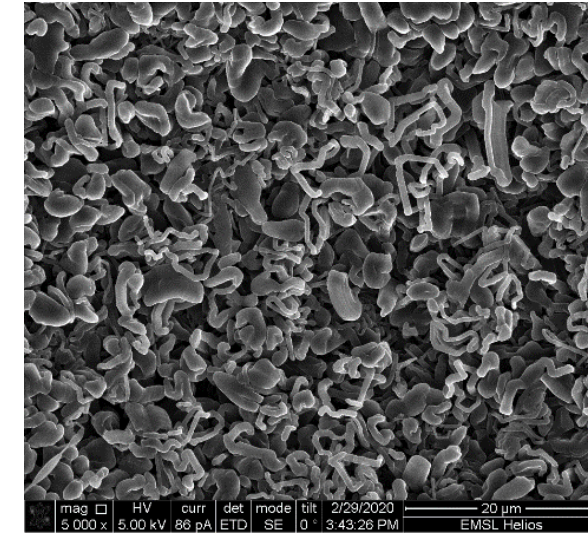
1 mAh cm<sup>-2</sup>



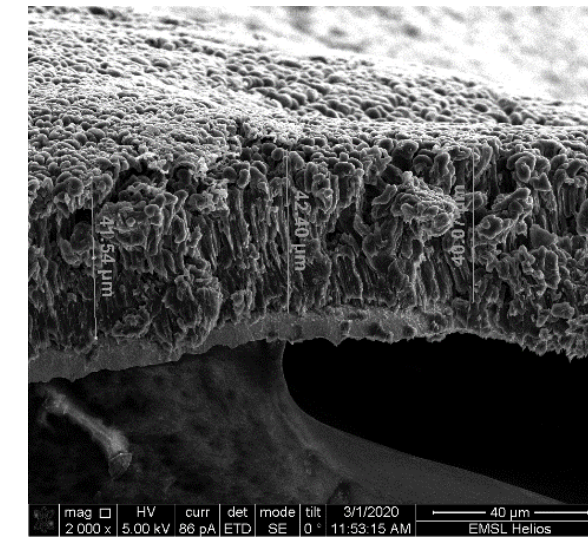
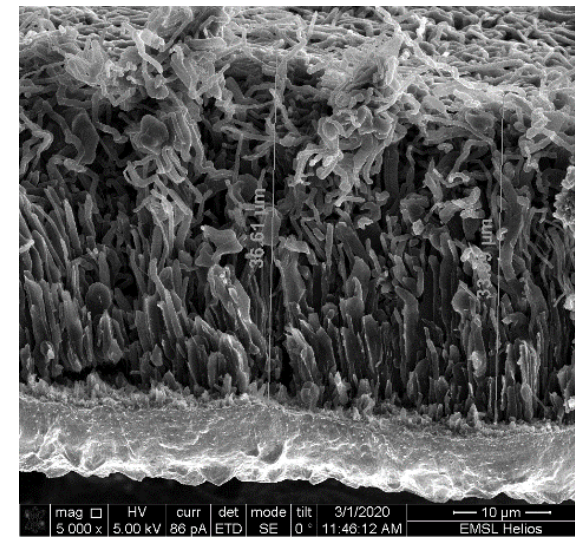
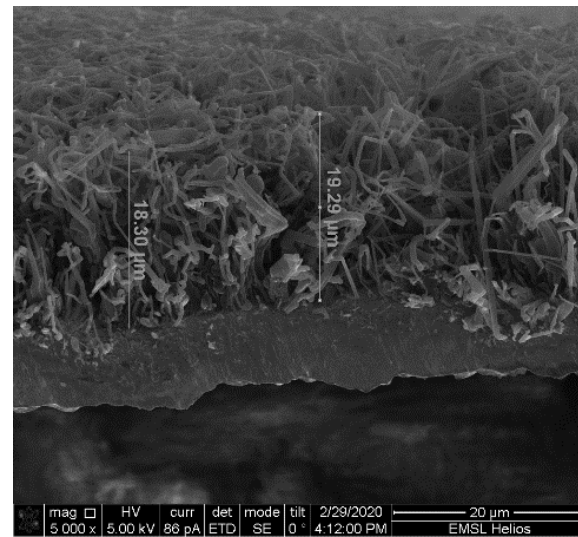
2 mAh cm<sup>-2</sup>



4 mAh cm<sup>-2</sup>



Cross-section view



- Increase in deposition capacity leads to larger and denser Li morphology.

## Responses to Previous Year Reviewers' Comments

- The three reviewers gave very good comments on this project last year. They did not ask issues to be addressed. We appreciated these reviewers for their very positive comments. We will continue to make efforts to achieve more successes in this project.

## Collaboration and Coordination with Other Institutions

- Dr. Bryant Polzin, Argonne National Laboratory
  - Provided coated NMC cathode sheets for testing.
- Dr. Kang Xu and Dr. Michael Ding, U.S. Army Research Laboratory
  - Conducted DSC measurements.
- Dr. Chongmin Wang, Pacific Northwest National Laboratory
  - Conducted cryo-TEM.

## Remaining Challenges and Barriers

- Coulombic efficiency of Li metal anode is not high enough during cycling.
- Cycling stability of Li metal batteries with high loading cathode.
- Li metal dimension or volume change during charging and discharging cycles.
- Solid-state polymer electrolytes only work well at high temperatures.

## Proposed Future Work

- Continue the development of low- to non-flammable hybrid polymer composite electrolytes and the evaluation in Li metal batteries.
- Achieve stable cycles for 4-V Li||NMC622 cells with hybrid polymer composite electrolytes.
- Characterize compositions of SEI layers and deposited Li films at different test conditions.

Any proposed future work is subject to change based on funding levels.

## Summary

- Developed hybrid polymer electrolytes.
  - With the optimal PQILE  $\text{Li}(\text{DME})_{0.7}\text{FSI-PEO}_{0.6}$ ,  $\text{Li}||\text{NMC333}$  cell has 79.2% capacity retention after 300 cycles with a cutoff voltage of 4.4 V.
  - With PISE plasticized by an ionic liquid, the quasi-solid state  $\text{Li}||\text{NMC333}$  cell has 74.4% capacity retention after 186 cycles with a cutoff voltage of 4.3 V.
- Developed an artificial SEI of Ag-LiF film for Li metal protection in liquid electrolyte.
  - Ag-LiF protected Li metal anode leads to uniform Li plating/stripping morphology, enables  $\text{Li}||\text{NMC333}$  cell to have >80% capacity retention for more than 500 cycles.
- Developed AN-based HCEs for high power Li metal batteries.
  - The optimal LVA shows high Li CE, excellent stability with Li metal, and superior cycling performance in Li metal batteries at high voltages and high current densities.
- Investigated deposited Li and SEI structure in conventional  $\text{LiPF}_6$ /carbonate electrolyte under different conditions.
  - Without VC the SEI is a multilayer structure, while with VC the SEI is a mosaic like structure.
  - The SEI changes from monolithic structure to mosaic structure with increasing current densities.
  - Increase in deposition capacity leads to larger and denser Li morphology.

## Acknowledgements

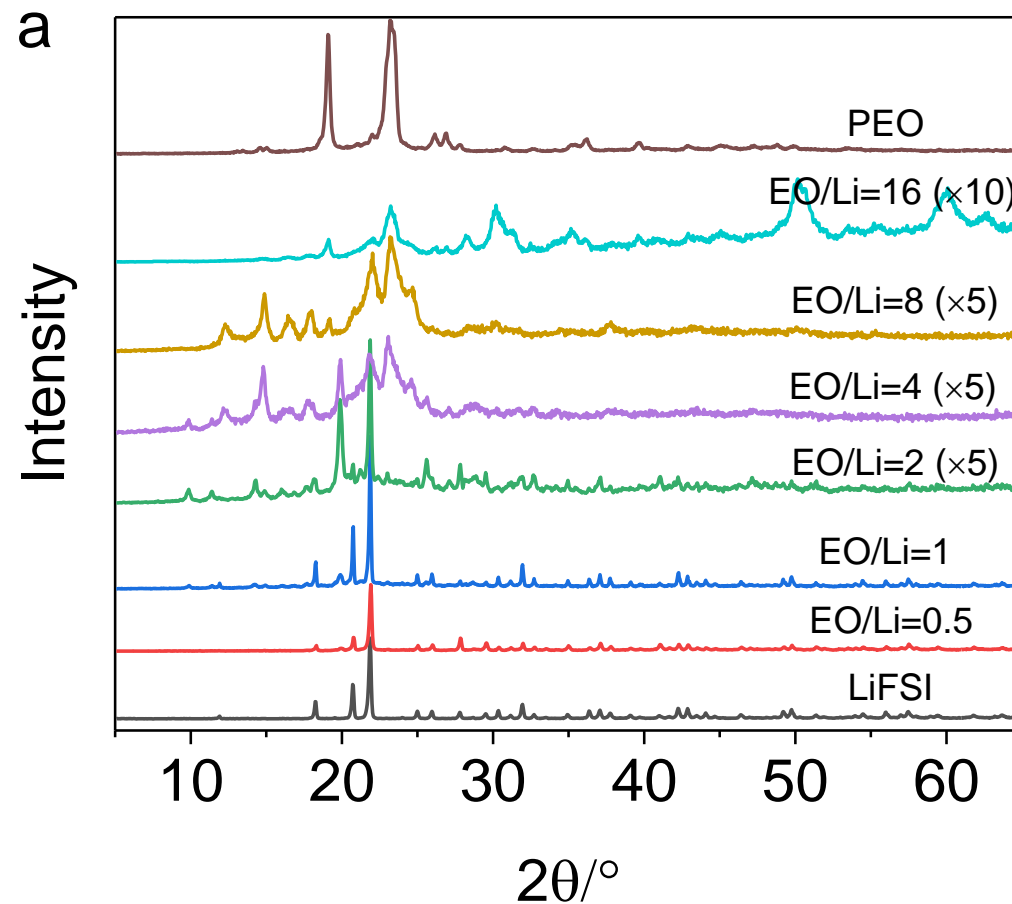
- Financial support from the DOE VTO BMR Program is greatly appreciated.
- DOE / BER / EMSL for microscopic and spectroscopic characterizations and computational calculations.
- Team Members:  
Haiping Wu, Hao Jia, Zhe Peng, Chongmin Wang, Yaobin Xu, Lianfeng Zou,  
Mark H. Engelhard, Patrick El-Khoury, Peiyuan Gao

# Technical Backup Slides

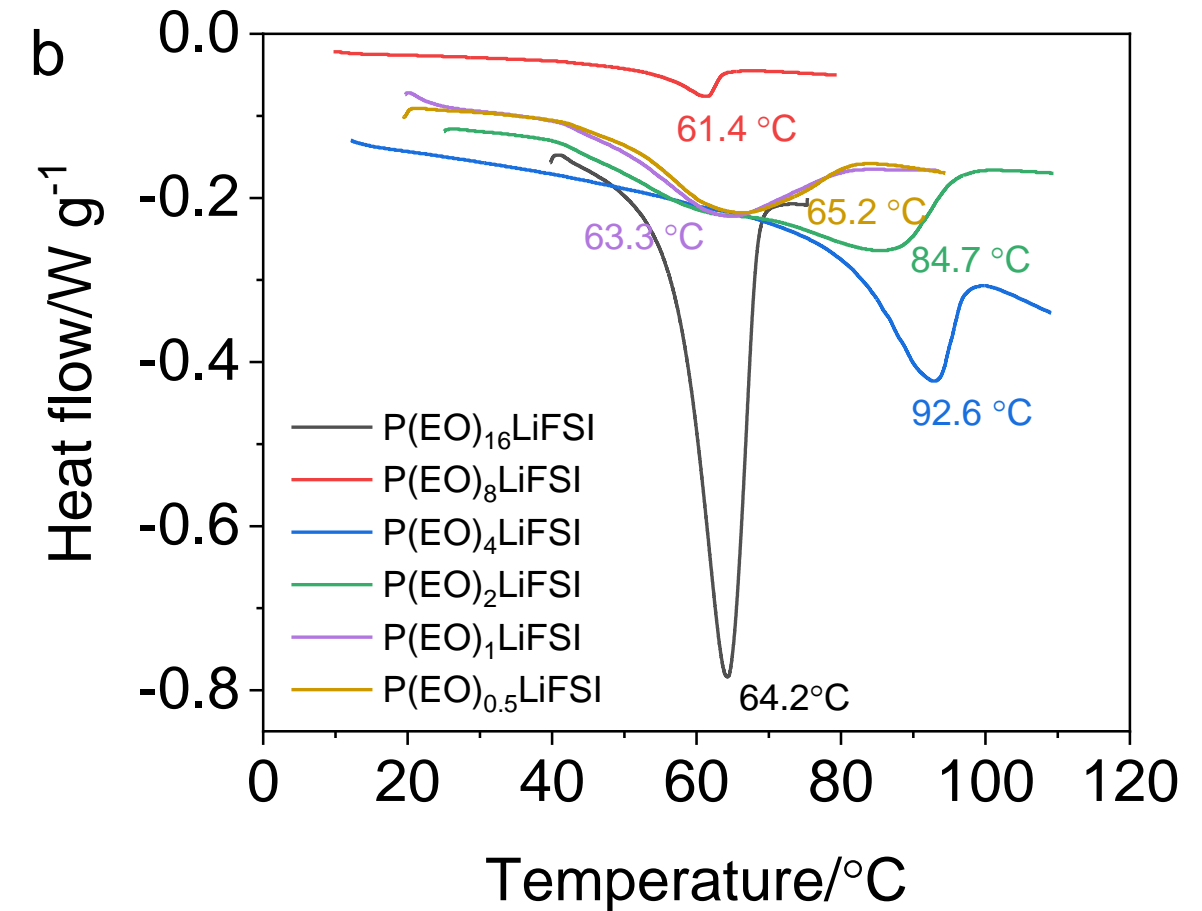


# Technical Accomplishments

## Structures and melting points of PISEs



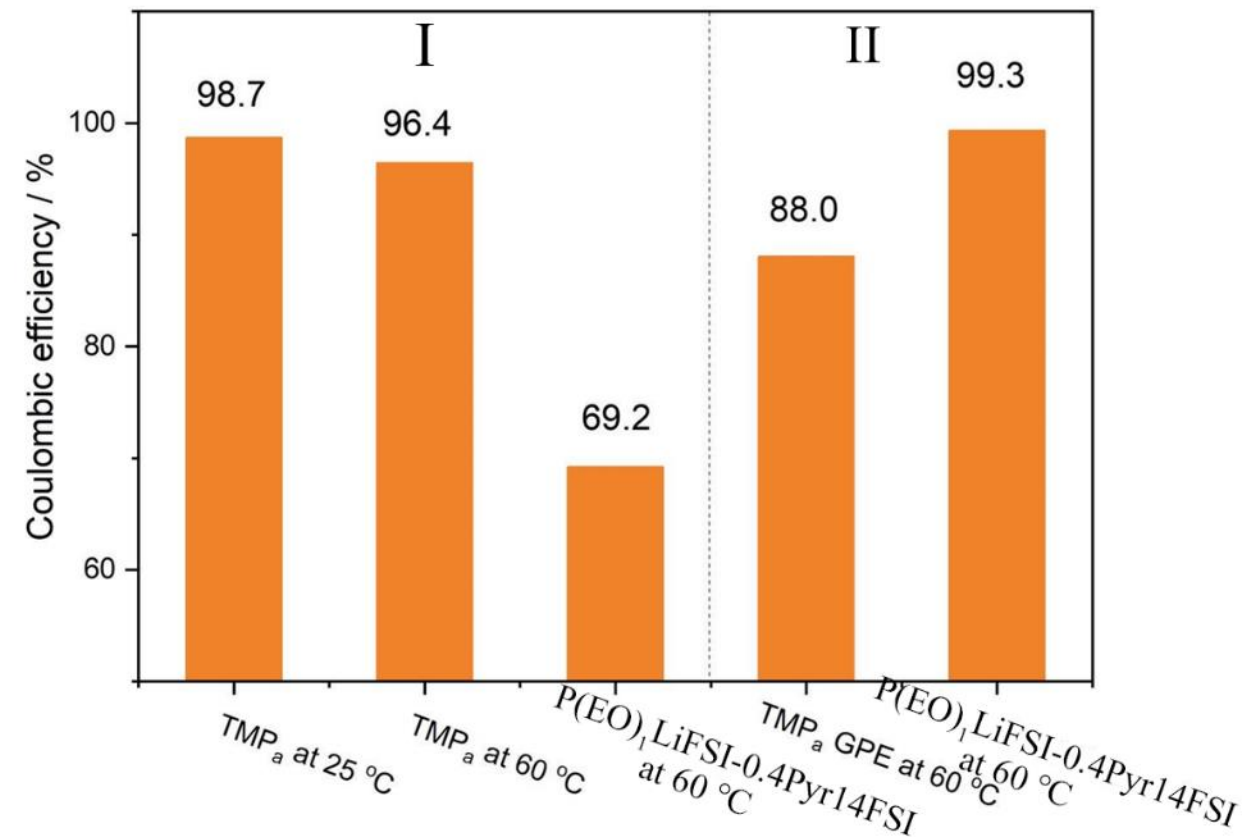
- Structure of PISE varies with EO/Li ratio.



- P(EO)<sub>1</sub>LiFSI has low melting point.

# Technical Accomplishments

## Average Li CE of hybrid polymer electrolytes from Li||Cu cells



### Testing protocols:

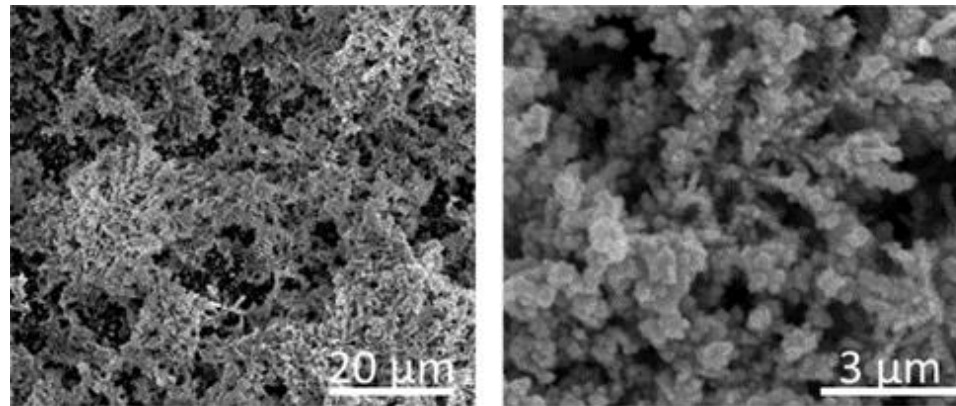
- Region I. Initial capacity of 5 mAh cm<sup>-2</sup>, cycling at 1 mAh cm<sup>-2</sup> for 9 cycles, then stripping all Li till 1 V, at 0.5 mA cm<sup>-2</sup>.
- Region II. Initial capacity of 1 mAh cm<sup>-2</sup>, cycling at 0.2 mAh cm<sup>-2</sup> for 9 cycles, then stripping all Li till 1 V, at 0.1 mA cm<sup>-2</sup>.

- CE is affected by test current density and cycled capacity.
- High Li CE of 99.3% can be achieved for quasi-solid state polymer electrolyte P(EO)<sub>1</sub>LiFSI-0.4Pyr<sub>14</sub>FSI at 60 °C.

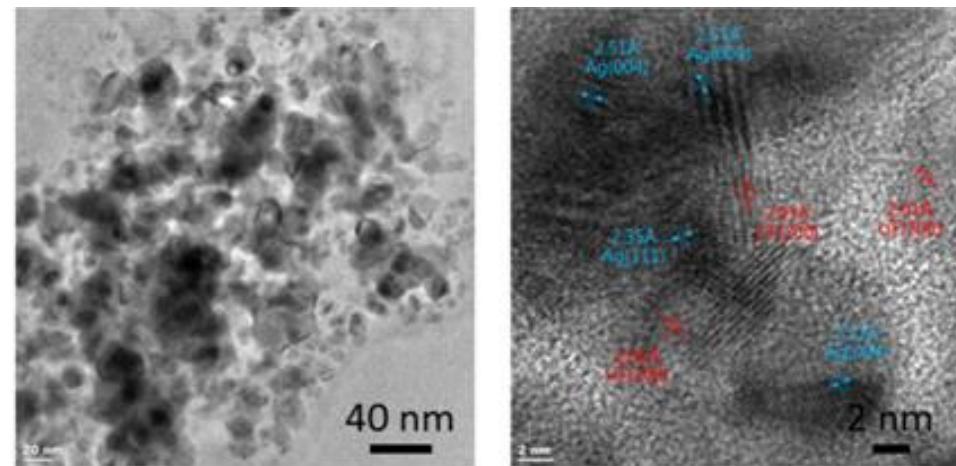
# Technical Accomplishments

Morphology and composition of Ag-LiF artificial SEI determined by SEM, TEM and XPS

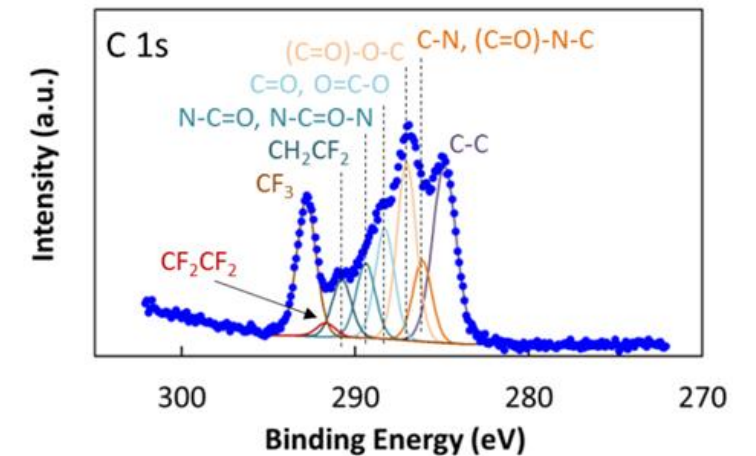
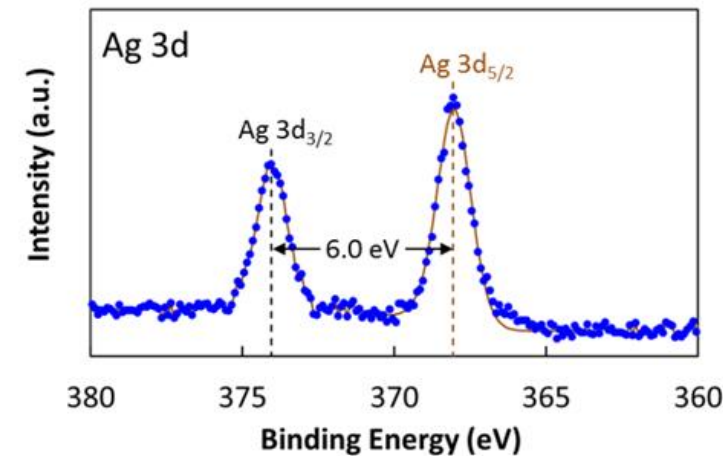
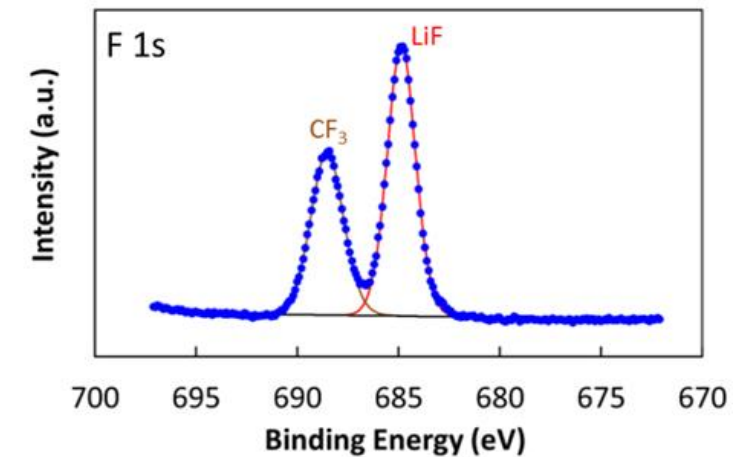
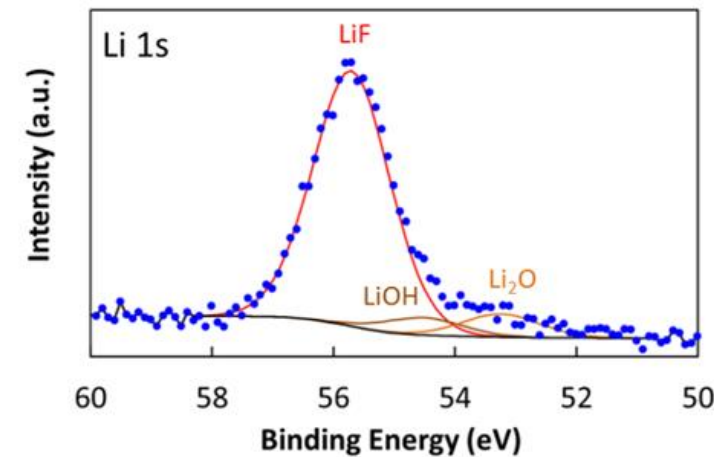
SEM



TEM



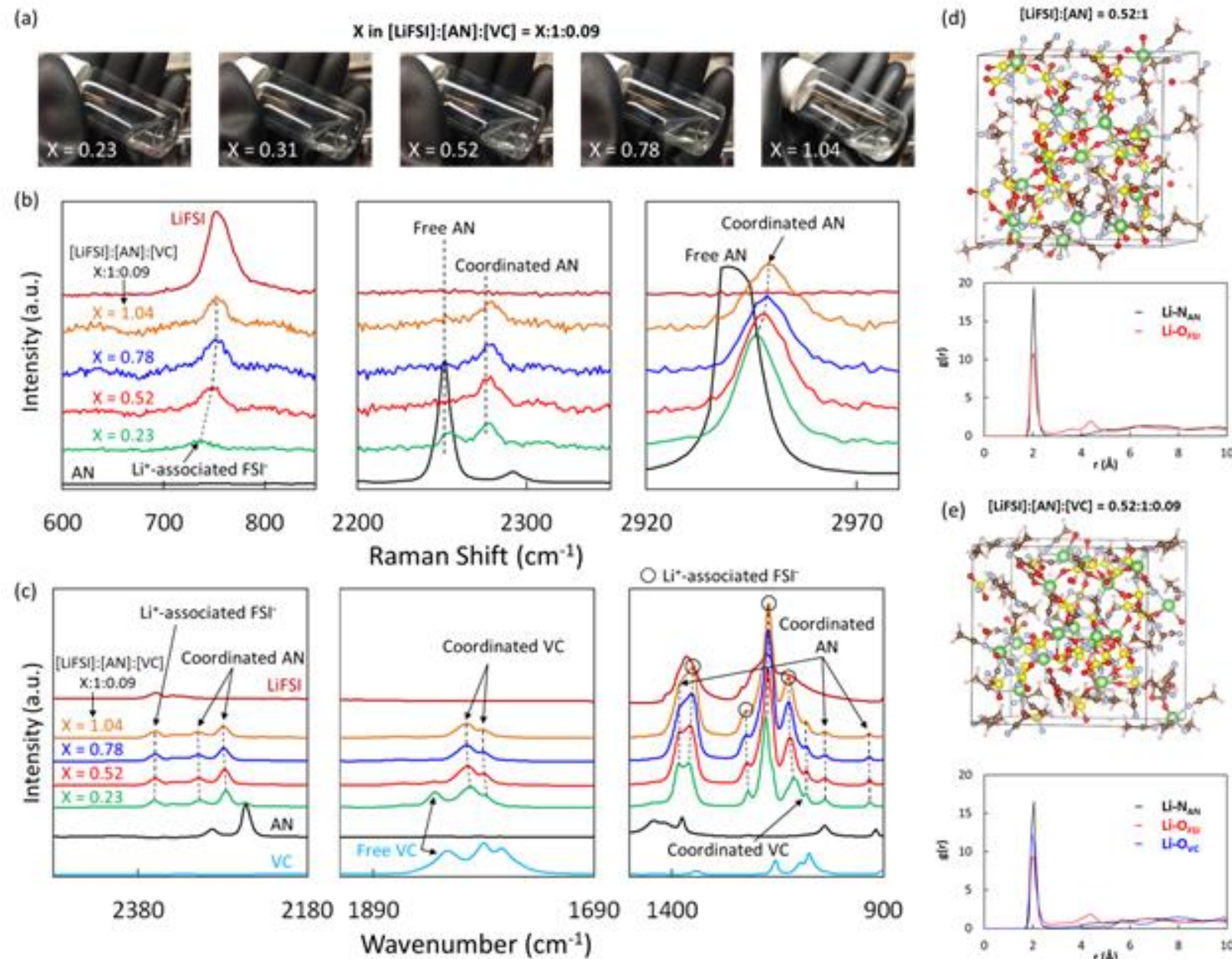
XPS



- TEM and XPS confirmed the successful synthesis of Ag-LiF artificial SEI on Li surface.

# Technical Accomplishments

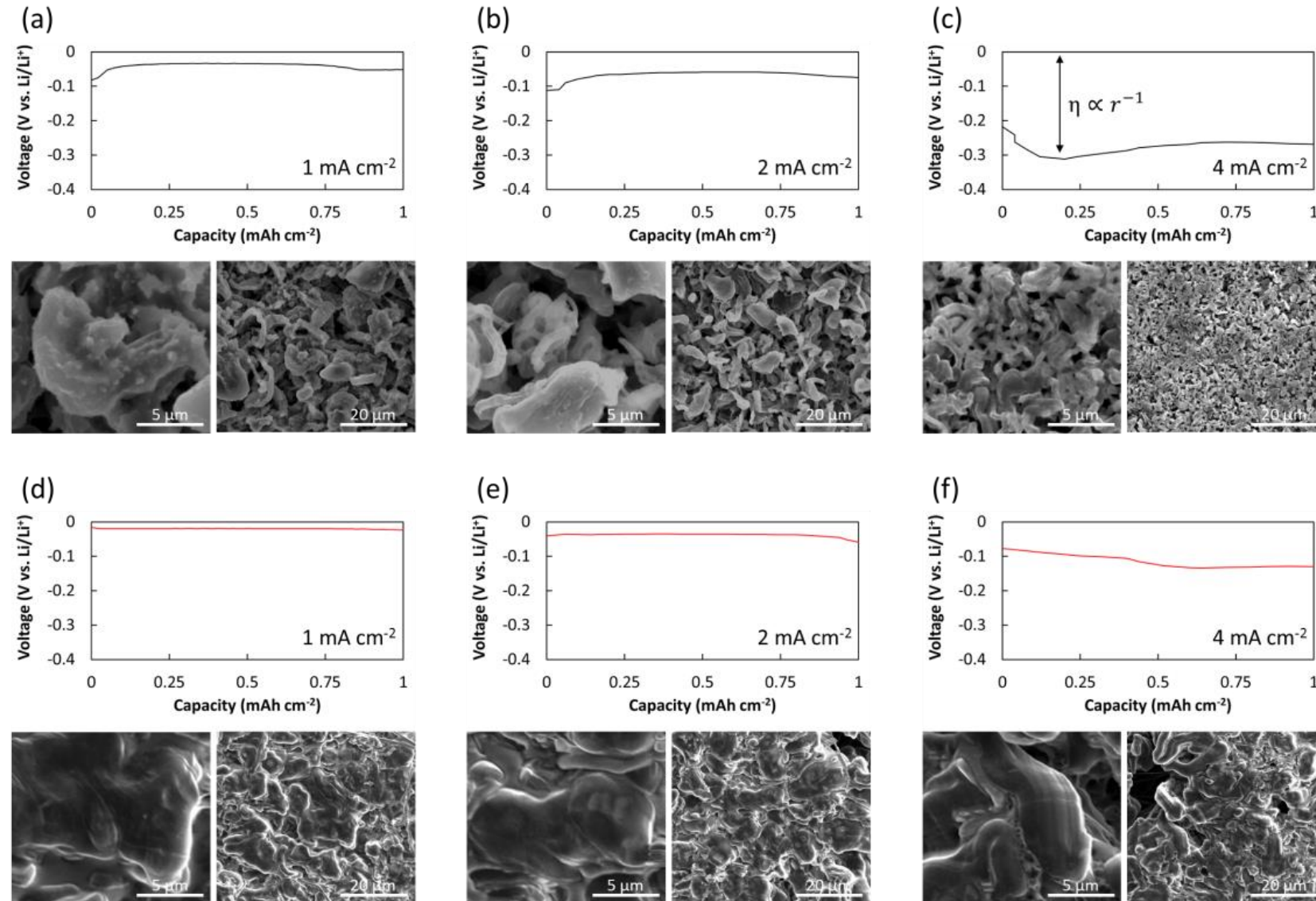
## Solvation structures of LiFSI-AN-VC HCEs via Raman spectra and simulation



- LiFSI-AN-VC (x:1:0.09 by mol) HCEs with  $x > 0.5$  show highly coordinated Li<sup>+</sup>-solvent pairs without free AN molecules.

# Technical Accomplishments

Voltage profiles of Li plating and SEM images of deposited Li in E-baseline ( $\text{LiPF}_6/\text{EC-DMC}+\text{FEC}$ ) and LAV ( $\text{LiFSI-AN-VC}$ ) at different current densities



E-baseline

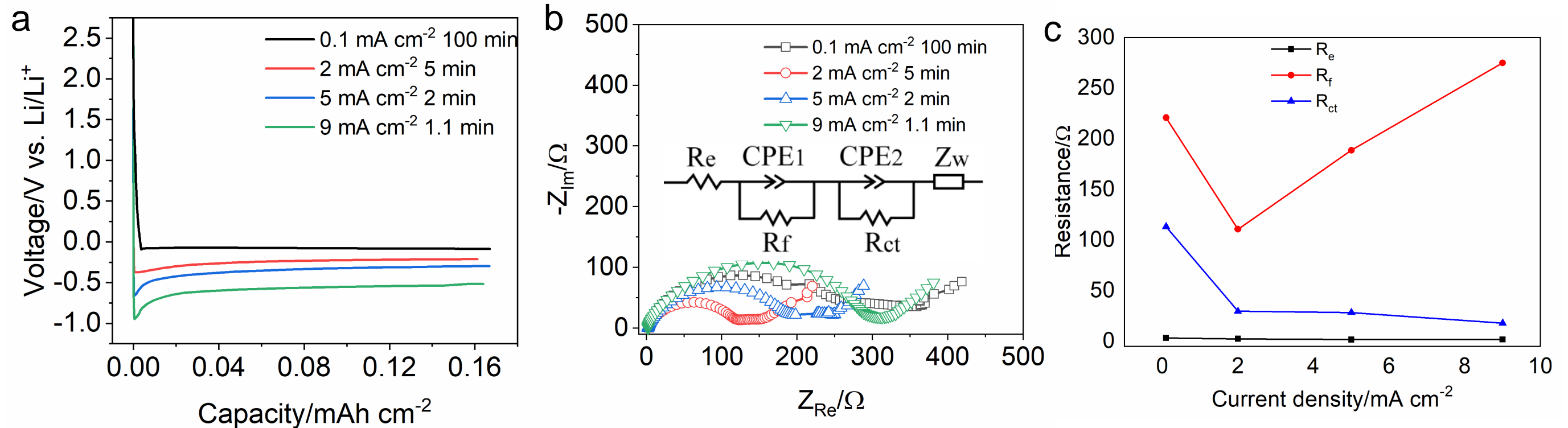
LAV

- LAV enables less overpotential during Li deposition and much more compact Li morphology.

# Technical Accomplishments

## Effect of deposition current density on nucleation overpotential and cell impedance

- Electrolyte of 1.2 M  $\text{LiPF}_6$  in EC:EMC (3:7 by wt.) + 5 wt.% VC was used in this study.



- Nucleation overpotential increases with increase of deposition current density.
- Increasing deposition current density results in a minimum passivation film resistance  $R_f$  at 2  $\text{mA cm}^{-2}$ .
- A proportional relationship between  $R_f$  and current density when current density ranges from 2 to 9  $\text{mA cm}^{-2}$ .